

Schrödinger equation solved for the hydrogen molecule with unprecedented accuracy

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The hydrogen molecule can be used for determination of physical constants and for improved tests of the hypothetical long range force between hadrons, which requires a sufficiently accurate knowledge of the molecular levels. For this reason, we have undertaken a project of significant improvements in theoretical predictions of H_2 and perform the first step, which is the solution of the nonrelativistic Schrödinger equation to the unprecedented accuracy of 10^{-12} . This will inspire, we hope, a parallel progress in the spectroscopy of the molecular hydrogen.

INTRODUCTION

The spectroscopy of simple atomic systems like hydrogen [1, 2], hydrogenic ions [3], muonic hydrogen [4], muonium, positronium has been used to determine fundamental physical constants and to test the quantum electrodynamic theory. Although experiments for more complicated atomic systems like helium or lithium can be as accurate as for hydrogen, the precision of theoretical predictions, at the moment, is not sufficient to determine physical constants, such as the fine structure constant α , the Rydberg constant (Ry), or the absolute value of the nuclear charge radius. In contrast, the hydrogen molecule, thanks to its simplicity, has already been used for the most accurate determination of the deuteron magnetic moment from NMR measurements [5], and for the studies of the unknown hypothetical fifth force at the atomic scale [6]. The precision achieved recently for transition frequencies, of an order of 10^{-4} cm^{-1} , has been verified by a series of measurements, which resulted in strong bounds on the fifth force. We will argue in this work, that it is possible to achieve 10^{-6} cm^{-1} accuracy for energy levels of the hydrogen molecule, which not only will improve tests of quantum electrodynamics theory and will put stronger bounds on the fifth force, but also will allow a resolution of the proton charge radius puzzle, which stands as a violation of the Standard Model of fundamental interactions [7].

The improvement in theoretical predictions for the hydrogen molecule can be achieved by the calculation of the yet unknown higher order $\alpha^4 \text{ Ry}$ quantum electrodynamics correction and by a more accurate solution of the nonrelativistic Schrödinger equation. This second improvement is performed in this work, while the calculation of the QED effects is in progress. The solution of the Schrödinger equation for the hydrogen molecule has been pursued since almost the beginning of the quantum mechanics theory. Over time, there have been many contributions to the development of methods with increased precision of theoretical predictions. Heitler and London

[8], James and Coolidge [9], Kołos and Wolniewicz [10], and many others have made their marks on the history of research on H_2 . Every breakthrough in the precision of theoretical predictions has been related to the progress in computational techniques. Fig. 1 illustrates the progress made over many decades in the precision of the dissociation energy D_0 for H_2 .

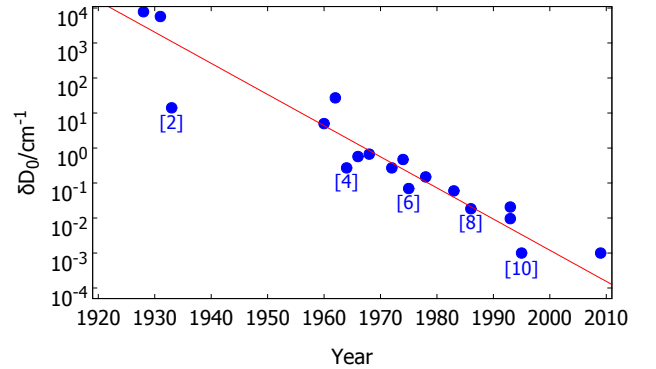


FIG. 1. The accuracy of theoretical predictions of dissociation energy D_0 of H_2 versus time, with the linear fit on the logarithmic scale.

Not always the results of calculations have been in agreement with measured values, which has questioned the validity of the theoretical approach. For example, in 1964 Kołos and Wolniewicz [11] solved variationally the nonadiabatic Schrödinger equation for the hydrogen molecule. The calculated dissociation energy appeared to be higher than the measured one [12], which was in contradiction with the variational principle. Five years later, Herzberg measured D_0 again with the accuracy increased to a few tenths of reciprocal centimeter and obtained a value higher than previously by 5 cm^{-1} in agreement with the Kołos and Wolniewicz predictions.

Further progress in theoretical predictions was related to the calculations of the leading relativistic corrections and to approximate QED effects [13–17]. Later on, due to rapid development of computer power, the methods

based on exponentially correlated Gaussian (ECG) functions have been developed both in the Born-Oppenheimer approximation [18] and in the direct nonadiabatic approach [19, 20]. Very recently, we have introduced a nonadiabatic perturbation theory (NAPT), which allowed the accuracy of about 10^{-3} cm^{-1} to be achieved for all the rovibrational levels of H_2 and isotopomers [18]. However, the complexity of NAPT in the higher order of electron-nucleus mass ratio [21] makes further improvements in accuracy quite complicated. For this reason, we propose another approach to the direct solution of the Schrödinger equation by the use of the special integration technique for explicitly correlated exponential functions and present its first results in this Letter. Over fifty years after Kolos and Wolniewicz, we approach the problem of solving the four-body Schrödinger equation, with the precision aim for D_0 at the level of 10^{-7} cm^{-1} .

THEORY

The main purpose of this work is to solve accurately the stationary Schrödinger equation $\hat{H}\Psi = E\Psi$ for a diatomic molecule with the nuclei of charge Z_A and Z_B and finite masses M_A and M_B

$$\hat{H} = -\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 - \frac{1}{2m_e}\nabla_1^2 - \frac{1}{2m_e}\nabla_2^2 + \frac{Z_A Z_B}{r_{AB}} + \frac{1}{r_{12}} - \frac{Z_A}{r_{1A}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{1B}} - \frac{Z_B}{r_{2B}}, \quad (1)$$

using the variational approach. The trial wave function

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) = \sum_{k=1}^K c_k \hat{S} \psi_{\{k\}}(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) \quad (2)$$

is expanded in properly symmetrized (\hat{S}), four-particle basis of exponential functions

$$\psi_{\{k\}} = \exp[-\alpha r_{AB} - \beta(\zeta_1 + \zeta_2)] r_{AB}^{k_0} r_{12}^{k_1} \eta_1^{k_2} \eta_2^{k_3} \zeta_1^{k_4} \zeta_2^{k_5}, \quad (3)$$

where $\zeta_i = r_{iA} + r_{iB}$ and $\eta_i = r_{iA} - r_{iB}$ are coordinates closely related to the prolate spheroidal coordinates of i -th electron, r_{ij} are interparticle distances, α and β are nonlinear variational parameters, and k_i are non-negative integers collectively denoted as $\{k\}$. For its resemblance to the electronic James-Coolidge function, we call this basis function *the nonadiabatic James-Coolidge* (naJC) function.

Application of the naJC function for evaluation of the matrix elements leads to a certain class of integrals. Efficient evaluation of these integrals has become feasible since the discovery of the analytic formulas [22, 23] and the corresponding recursive relations [24, 25]. For example, the master integral, which is the starting point for

the recursions, can be expressed in the following form

$$\int \frac{dV}{(4\pi)^3} \frac{e^{-t r_{AB}} e^{-u(r_{1A}+r_{1B})} e^{-w(r_{2A}+r_{2B})}}{r_{AB} r_{12} r_{1A} r_{1B} r_{2A} r_{2B}} = \frac{1}{4uw} \left[-\frac{\ln\left(\frac{2u}{t+u+w}\right)}{t-u+w} - \frac{\ln\left(\frac{2w}{t+u+w}\right)}{t+u-w} + \frac{\ln\left(\frac{2uw}{(u+w)(t+u+w)}\right)}{t+u+w} + \frac{\ln\left(\frac{2(u+w)}{t+u+w}\right)}{t-u-w} \right]. \quad (4)$$

The integrals with additional positive powers of interparticle distances are obtained by straightforward algebraic recursion relations, which nevertheless are too long to be written explicitly here. All of them can be derived from a single fourth-order differential equation [25], which is satisfied by the general four-body integral, and are expressed in terms of logarithmic and rational functions. Details of this recursion method will be described elsewhere.

NUMERICAL RESULTS

Results of our calculations for H_2 are presented in Tab. I in the form a sequence of energies resulting from increasing length (K) of expansion (2). The selection of K was made on the basis of the saturation of consecutive 'shells' limited by $\sum_{k=1}^5 k_i \leq \Omega$ with k_0 fixed at 30. The observed regular convergence, obeying the inverse power law, permits a firm extrapolation to the complete basis set as well as an estimation of the uncertainty. The final value agrees well with the previous estimation of $-1.164\,025\,030\,84(6)$ a.u. obtained by Bubin et al. [20] but has a significantly smaller uncertainty.

TABLE I. Convergence of the Schrödinger equation eigenvalue E (in a.u.) and of the corresponding dissociation energy D_0 (in cm^{-1}) for H_2 with the size of the basis set.

Ω	K	E	D_0
10	36642	-1.164 025 030 821 4	36 118.797 732 57
11	53599	-1.164 025 030 870 9	36 118.797 743 43
12	76601	-1.164 025 030 880 4	36 118.797 745 52
13	106764	-1.164 025 030 882 5	36 118.797 745 97
∞	∞	-1.164 025 030 884(1)	36 118.797 746 3(2)

Further increase in the accuracy of eigenvalue of the four-body Schrödinger equation is feasible, but the problem we face is the lack of the parallel code in multi-precision arithmetics for the LDL^T matrix decomposition with pivoting, which results in a long computation time. However, current uncertainties in the electron-proton (proton-deuteron) mass ratio and in the Rydberg constant are much more significant than those due to numerical uncertainties. For example, the CODATA 2014

[26] electron-proton mass ratio has a relative uncertainty of $9.5 \cdot 10^{-11}$, which affects the eigenvalue of H_2 at the level of $4.3 \cdot 10^{-12}$ a.u. and the corresponding dissociation energy at $8.5 \cdot 10^{-7} \text{ cm}^{-1}$. Similarly, the current uncertainty in the Rydberg constant affects the conversion of D_0 value from a.u. to reciprocal centimeters at the level of $2.1 \cdot 10^{-7} \text{ cm}^{-1}$. This indicates, that one cannot exclude the possibility, to determine the electron-proton mass ratio from future high precision studies of H_2 .

CONCLUSIONS

The approach based on explicitly correlated exponential functions and the obtained results pave the way to a significant progress in the theory of the hydrogen molecule. A similar precision for nonrelativistic energies can be achieved for any other molecular level of H_2 , D_2 , HD , and HeH^+ . Considering the leading relativistic corrections, they can be expressed in terms of an expectation value with the nonrelativistic wave function, so their evaluation does not pose a significant problem, and they have already been calculated in the BO approximation. The leading quantum electrodynamics effects are more complicated due to Bethe logarithm contribution, which involves the logarithm of the nonrelativistic Hamiltonian. Its calculation beyond the BO approximation might be problematic. However, much more challenging is the calculation of the higher order $\alpha^4 \text{ Ry}$ contribution, which apart from hydrogen, was calculated only for He atom. Its magnitude can be estimated by $2\alpha^2$ times the known leading relativistic correction to D_0 of 0.5 cm^{-1} , which gives $5 \cdot 10^{-5} \text{ cm}^{-1}$. It would be probably necessary to approximately evaluate also $\alpha^5 \text{ Ry}$ corrections to achieve 10^{-6} accuracy, as it is enhanced by the presence of $\ln \alpha^{-2}$ factors.

At the level of accuracy of 10^{-6} cm^{-1} , the proton charge radius, which contributes about $1.2 \cdot 10^{-4} \text{ cm}^{-1}$ to the dissociation energy of H_2 , can be determined with 0.5% precision, provided that equally accurate measurement is performed. This certainly will resolve the proton charge radius discrepancy, which is at the level of 4%, and will open a new era in precision quantum chemistry. Regarding the tests of hypothetical forces, which are beyond those in the Standard Model, the atomic scale is the natural region for the long range hadronic interactions. Moreover, it has recently been shown that vibrational levels of the hydrogen molecule [27] are particularly sensitive to the interactions beyond the Coulomb repulsion between nuclei. So any deviation between hopefully improved theoretical predictions and the experiment may signal a new physics.

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